REPORT DOCUMENTATION PAGE

Form Approved
OMB NO. 0704-0188

1. AGENCY USE ONLY (Leave Blank)	2. REPORT DATE **2005/08/24**	3. REPORT TYPE AND DATES COVERED **Final**

4. TITLE AND SUBTITLE

Final Progress Report: Integrated Optical Pumping of Cr & & Ti-doped spahhire substrates with III-V Nitride Materials

5. FUNDING NUMBERS

DAAD19-00-1-0489

6. AUTHOR(S)

John Muth

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)

NC State University, ECE Dept., Box 7911 Raleigh NC 27695

8. PERFORMING ORGANIZATION REPORT NUMBER

9. SPONSORING / MONITORING AGENCY NAME(S) AND ADDRESS(ES)

U. S. Army Research Office
P.O. Box 12211
Research Triangle Park, NC 27709-2211

10. SPONSORING / MONITORING AGENCY REPORT NUMBER

40283.1 - EL

11. SUPPLEMENTARY NOTES

The views, opinions and/or findings contained in this report are those of the author(s) and should not be construed as an official Department of the Army position, policy or decision, unless so designated by other documentation.

12 a. DISTRIBUTION / AVAILABILITY STATEMENT

Approved for public release; distribution unlimited.

12 b. DISTRIBUTION CODE

13. ABSTRACT (Maximum 200 words)

The goal of this proposal was to investigate the potential advantages of integrating III-V nitride structures on doped sapphire substrates and doped sapphire waveguide structures. III-V Nitride structures are typically grown on undoped synthetic sapphire or silicon carbide neither of which efficiently luminescence. However, Cr:Sapphire and especially Ti:Sapphire are very useful solid state laser materials used in ruby lasers (694 nm) and tunable (660-1100) Ti:sapphire lasers respectively. Blue and Green III-V nitride materials overlap the absorption bands of the Cr and Ti dopants in sapphire, thus very efficient optical pumping powers on the order of several watts and supporting infrastructure to remove the heat is required. By confining the optical pump energy to the waveguide, simultaneous pump and signal beam confinement could potentially lead to a reduction in lasing threshold. Utilizing the red emission from the Cr in the sapphire could also permit the construction of white light LEDs. Ultimately, an integrated III-V Nitride optical pump for Ti:Sapphire could lead to the development of ultra compact tunable vibronic lasers for spectroscopy applications such as chemical and biological sensing.

14. SUBJECT TERMS **Gallium Nitride, Laser, waveguide**	15. NUMBER OF PAGES **12**
	16. PRICE CODE

17. SECURITY CLASSIFICATION OR REPORT	18. SECURITY CLASSIFICATION ON THIS PAGE	19. SECURITY CLASSIFICATION OF ABSTRACT	20. LIMITATION OF ABSTRACT
UNCLASSIFIED	UNCLASSIFIED	UNCLASSIFIED	UU

NSN 7540-01-280-5500

Standard Form 298 (Rev.2-89)
Prescribed by ANSI Std. 239-18
298-102

Enclosure 1

01 Sep 00 - 28 Feb 05 40283.1

Final Progress Report: Integrated Optical Pumping of Cr& Ti-Doped Sapphire Substrates with III-V Nitride Materials

By

Dr. John Muth
ECE Dept
NC State University
muth@unity.ncsu.edu
919 513 2982

Submitted to:
Dr. William Clark, Division Chief
Electronics Division
Army Research Office

Statement of the Problem Studied

The goal of this proposal was to investigate the potential advantages of integrating III-V nitride structures on Doped Sapphire substrates and doped sapphire waveguide structures. III-V Nitride structures are typically grown on undoped synthetic sapphire or silicon carbide neither of which efficiently luminescence. However, Cr: Sapphire and especially Ti: Sapphire are very useful solid state laser materials used in ruby lasers (694 nm) and tunable (660-1100) Ti: Sapphire lasers respectively. Blue and Green III-V nitride materials overlap the absorption bands of the Cr and Ti dopants in sapphire, thus very efficient optical pumps should result. In bulk solid state lasers relatively high optical pumping powers on the order of sever watts are required, and supporting infrastructure to remove the heat is required. By confining the optical pump energy to the waveguide, simultaneous pump and signal beam confinement could potentially lead to a reduction in lasing threshold. Utilizing the red emission from the Cr in sapphire could also permit the construction of white light LEDs. Ultimately, an integrated III-V Nitride optical pump for Ti:Sapphire could lead to the development of ultra compact tunable vibronic lasers for spectroscopy applications such as chemicals and biological sensing.

Specific goals of the program from the original proposal:

Part 1

1. Deposition of GaN/InGaN heterostructures and quantum Wells on Ti and Cr- doped sapphire substrates by MOCVD.
2. Characterization of doped sapphire/InGaN structures by PL to simulate electrical injection by laser or LED device structures

Part 2

1. Development of Doped sapphire Waveguide Structures
    a. Cr doping by high temperature diffusion method
    b. Ti: doping by high temperature diffusion
2. Characterization of Diffused waveguides
3. Growth of Wide band gap semiconductor on diffused waveguides

Part 3

1. Growth of electroluminescent device on doped sapphire waveguide material

In general these goals were mostly achieved.

LED devices were successfully grown on Cr:doped sapphire substrates, and diffused Cr:Sapphire waveguides were achieved. The diffused waveguides were characterized by the prism coupling method. Material deposition was also performed on doped Cr: Sapphire waveguides. However, GaN laser structures were not integrated into the waveguide structures. This was largely due with the difficult of achieving GaN lasers in a university environment due to the high degree of materials optimization that is required.

Summary of the Most Important Results:

The feasibility of growing high quality GaN on Chromium doped sapphire was demonstrated.

(InGaN was also grown on Ti:Sapphire substrates with high material quality obtained, but results not shown here for brevity.)

As shown in the figures below GaN devices were grown on both Sapphire and Ruby (Cr:Sapphire substrates). This resulted in dual wavelength emission at 470 and 694 nm. The mechanism for the emission is described in Figure 1 below. The growth was performed by Mason Reed in Dr. S.M. Bedair laboratory, the characterization was performed by Andrew Oberhofer in Dr. Muth's laboratory.

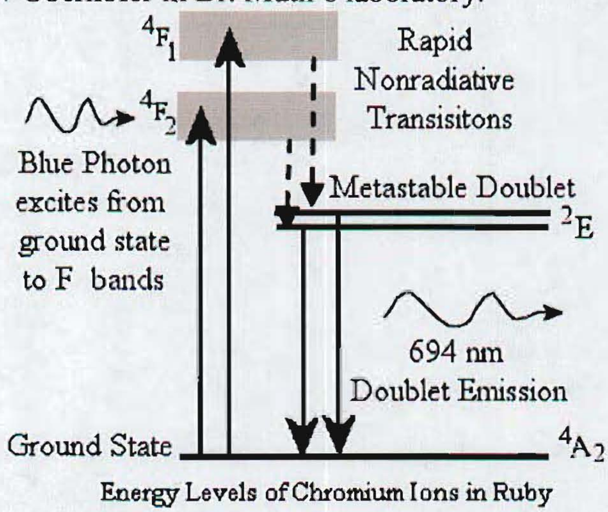


Figure 1. An energetic blue photon excites an electron from the ground state to the broad absorption bands (4F1 or 4F2). Fast non radiative recombination de-excites the electron to one of two long lived metastable states in the 2E doublet. The electron then decay to the ground state (4A2) emitting a spectrally narrow photon at 694 nm. Blue photons that are not absorbed by the Cr ion are also emitted from the LED.

The device structure and IV characteristics are shown in Figure 2 and 3

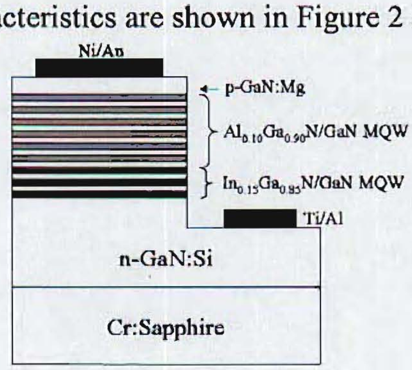


Figure 2. Schematic diagram of the InGaN LED epitaxially grown on Cr:sapphire substrate.

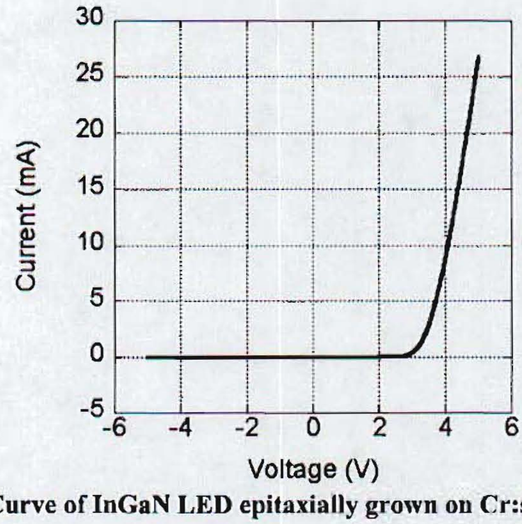


Figure 3. Current Voltage Curve of InGaN LED epitaxially grown on Cr:sapphire substrate.

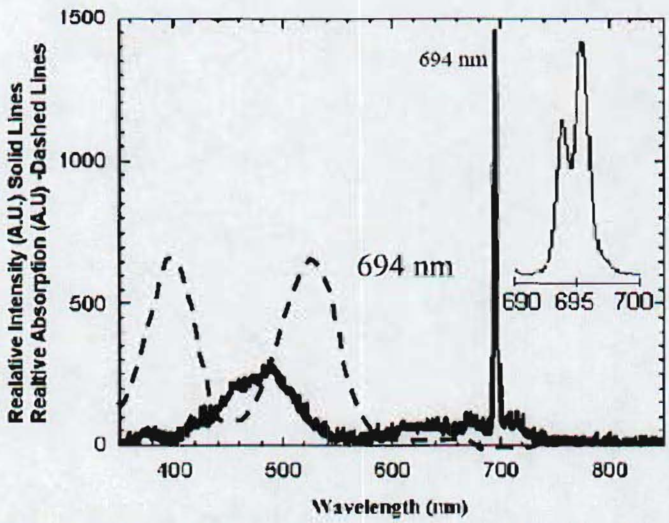


Figure 4. Dashed line is absorption spectrum of 0.05% Cr:sapphire substrate. Solid line is the spectrum of blue and red light emitted by InGaN LED epitaxially grown on Cr:sapphire substrate. The light was collected through the Cr:sapphire substrate. The inset shows the characteristic doublet (R1 and R2) of the ruby emission line at 694

A picture of the Gallium Nitride LED grown on doped substrates is shown in Figure 5. Note the deep red color of the ruby substrate.

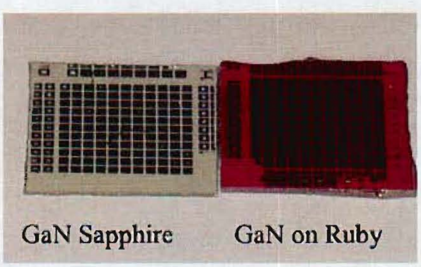
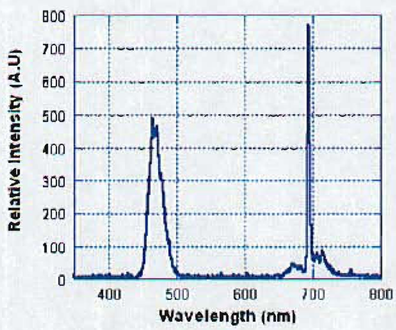
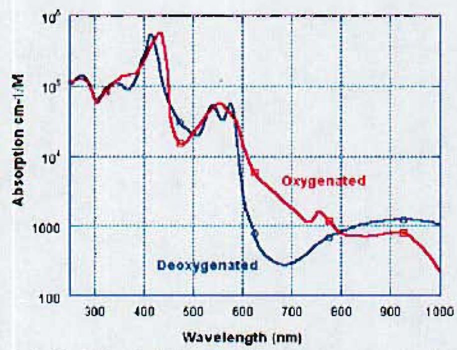


Figure 5. Pictures of GaN LEDs grown on undoped and doped sapphire substrates.

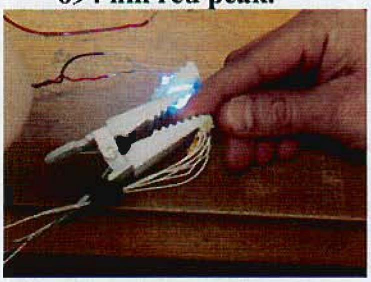
To explore the possible uses of this a Pulse Oximeter device was built using a hybrid GaN/Ruby device to measure the oxygen content in blood.Since the 694 nm line is coincident with the change in absorption that occurs when the hemoglobin of blood cells absorbs oxygen it can be used to make ratiometric measurements of the oxygen content of blood. To explore this concept, a tem of students in the biomedical instrumentation class built a working pulse oximeter based on this 470 nm and 694 nm InGaN/Ruby type of emitter.



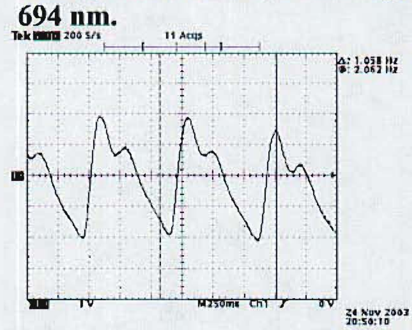
a) Emission of Blue LED exciting Ruby consisting of a 470 nm blue peak, and 694 nm red peak.



b) Optical Absorption oxygenated and deoxygenated blood, with large change at 694 nm.



b) Pulse oximetry idea implemented with blue LED and Cr Doped Sapphire.



Experimental data using InGaN/Ruby pulse oximetry built by a student design team in medical instrumentation class. Peaks correspond to fresh oxygenated blood being pumped through finger.

Figure 6. Pulse oximeter built to demonstrate potential sensor based on InGaN doped sapphire technology.

The feasibility of fabricating Cr:Sapphire waveguides by diffusion was demonstrated.

Ti:doped waveguides were also fabricated, but were of poorer quality due to problems maintaining the proper Oxygen stoichiometry and positioning the Ti: on the correct lattice site.). **The formation of multimode waveguides was also accomplished by deposition of Cr: doped sapphire and subsequent annealing.** It was hard to obtain multimode waveguides by thermal diffusion. **Prism coupling was used to characterize the films.** A summary of the Cr:Sapphire research is shown below. A preliminary growth of ZnO was performed on a Cr:apphire waveguide sample.

C-sapphire is a uniaxial crystal. By using transverse electric (TE) and transverse magnetic (TM) polarized light, the ordinary and extraordinary modes are excited respectively. The TE mode spectrum of Cr doped sapphire waveguide is shown in Fig. 7 (a). Two sharp reflectivity dips of guided modes of the Cr doped sapphire waveguide are identified as the modes of TE_0 and TE_1. Also, the substrate radiation modes are shown in Fig. 7(a). The TM coupling curve of the laser beam into Cr doped sapphire waveguide is shown in Fig. 7(b). TM_0 mode is obtained. These indicate that the presence of the Cr metal locally increased the refractive index of the sapphire resulting in a graded index waveguide due to diffusion.

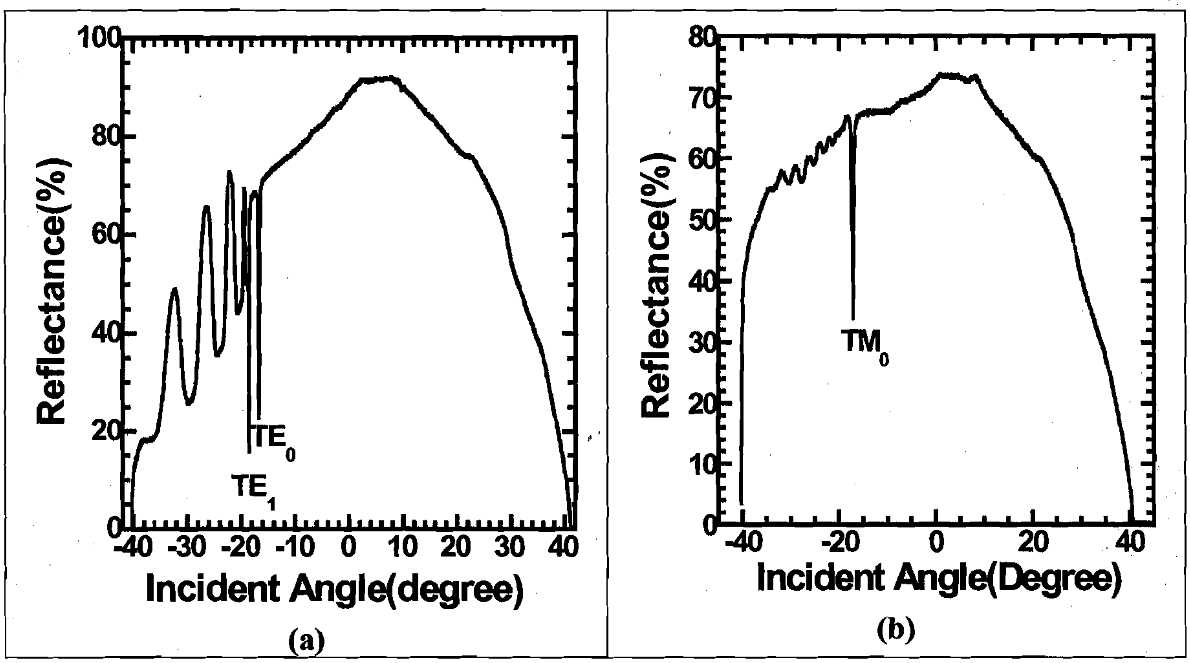


Figure 7 (a) TE coupling curve of the laser beam into Cr doped sapphire waveguide
(b) TM coupling curve of the laser beam into Cr doped sapphire waveguide

In order to obtain the knowledge of the refractive index of Cr doped sapphire waveguide, WKB method is applied due to the graded refractive index change. The characteristic equation for the *m*th–order mode for the graded waveguide is given by

$$k \int_0^{x_t(m)} [(n^2(x) - N^2(m)]^{\frac{1}{2}} dx = m\pi + \phi_a + \phi_s$$

And

$$n(x_t(m)) = N(m)$$

Where N(m) is the effective index of the mth-order mode. x_t is the turning point of the WKB method. $2\phi_a, 2\phi_s$ are the phases shift at the film-air and film-substrate.[31]
Also, n(x) is given by[32,33]

$$n(x) = n_s + \Delta n \exp(-\frac{x}{d})$$

Where n_s is the refractive index of the substrate, d is the diffusion depth.

By using prism coupling method for TE polarized light at wavelength of 457.9 nm, three modes are found. The effective indices change with doping depth is extracted based on inverted WKB method and shown in Fig. 3-16. The Cr^{3+} ions concentration exponentially decays. The doping depth is about 2.2μm. Based on the relationship between the diffusion depth and the diffusion coefficient of D,[34]

$$d = 2(Dt)^{\frac{1}{2}}$$

then the diffusion coefficient of Cr in sapphire is 3.3×10^{-16} m^2/sec.

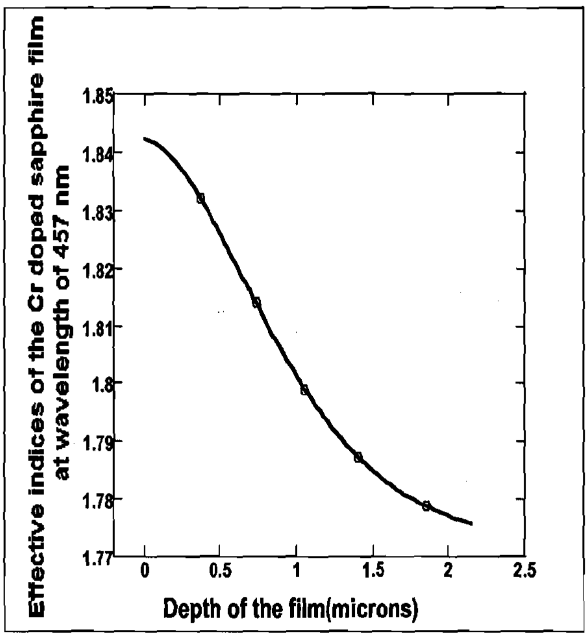


Figure 8. The effective indices change as a function of doping profile

In order to study the surface morphologies of the Cr doped sapphire, AFM images of the bulk sapphire and Cr diffused sapphire in the size of 5 μm by 5 μm scans are taken and shown in Fig. 9 (a) and (b). The root mean square values (RMS) of the surface roughness of sapphire and Cr diffused sapphire are 0.68 nm and 0.73 nm respectively. . This indicates the materials growth on Cr diffused sapphire is applicable.

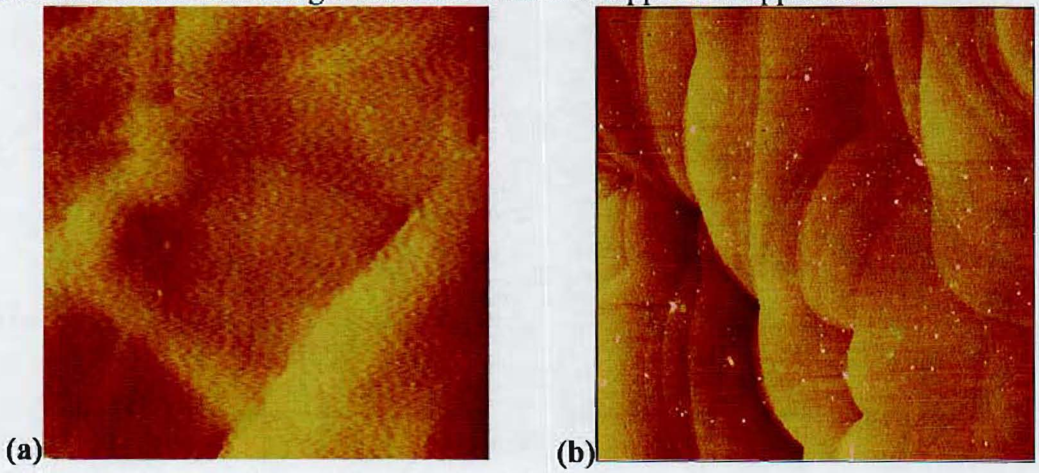


Figure 9. (a) AFM image of bulk sapphire in the size of 5 μm by 5 μm scan
(b) AFM image of Cr diffused sapphire in the size of 5 μm by 5 μm scan

The transmission spectrum of Cr doped sapphire was taken with a Lambda9 ultraviolet- visible-near infrared (UV-VIS-NIR) absorption spectrophotometer. The transmission spectrum is shown in Fig 10 (a). There is about 78% of transmission of the Cr doped sapphire from 300 nm to 800 nm. Also, based on the transmission data, the absorbance spectrum of Cr doped sapphire waveguide as a function of wavelength is plotted in Fig. 10 (b). The two broad absorption bands at wavelengths of around 424nm and 566 nm are due to transitions from the $^4A_2$ ground state of Cr^{3+} to the excited $^4F_2$ and $^4F_1$ levels. This indicates that the Cr ions were incorporated into sapphire in the trivalent state resulting in strong emission at 694 nm.

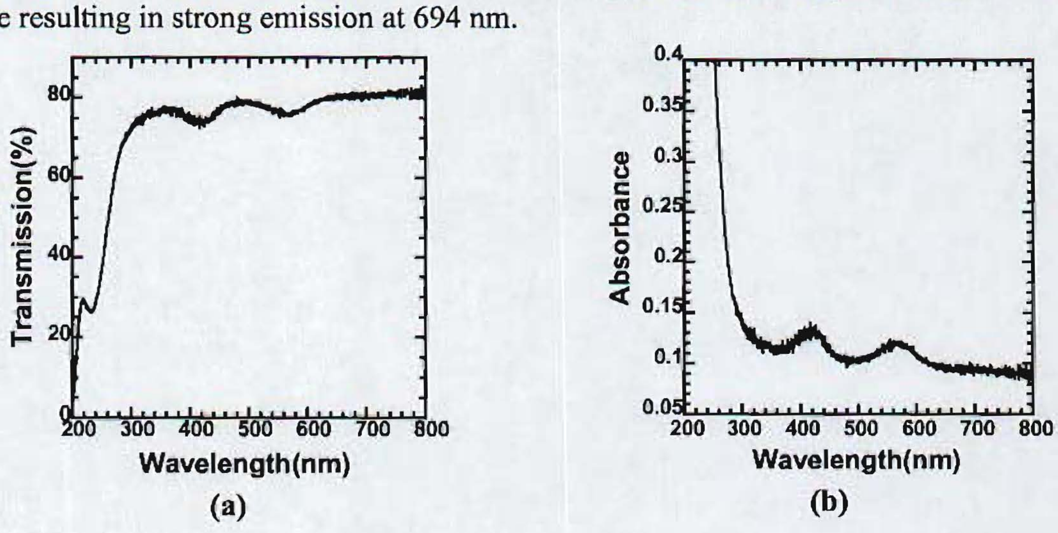


Figure 10 (a) Transmission spectrum of Cr doped sapphire waveguide
(b) Absorbance spectrum of Cr doped sapphire waveguide

Fig. 11 shows the cathodoluminescence spectrum of the Cr diffused waveguide. The strong emission of R_1 line at 694 nm is due to the transition from the E level to the grand state of $^4A_2$. This indicates that the Cr ions were incorporated into sapphire in the trivalent state resulting in strong emission at 694 nm.

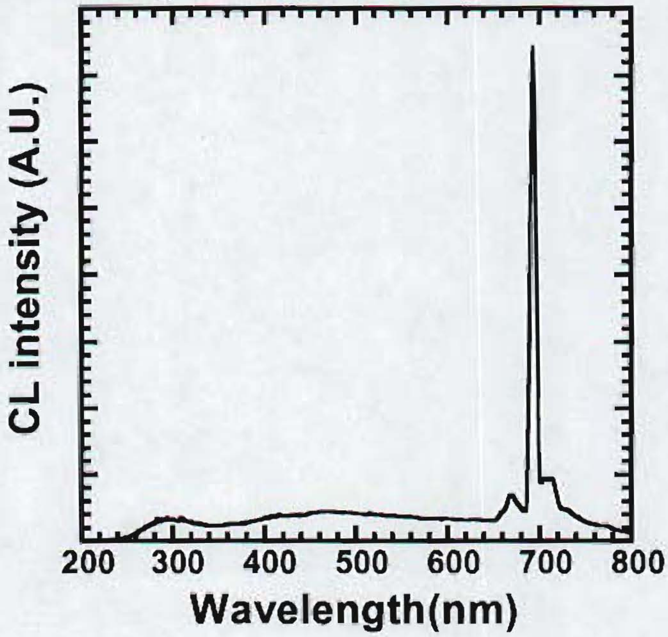


Figure 11. Cathodoluminescence of Cr diffused sapphire waveguide

By using a lensed-fiber integrated with a 2 mm diameter of ball lens coupling system, light is coupled into the Cr-diffused waveguide from the input to the output end face at 632.8 nm shown in Fig. 12. This confirms that the high quality optical Cr-diffused waveguide is fabricated.

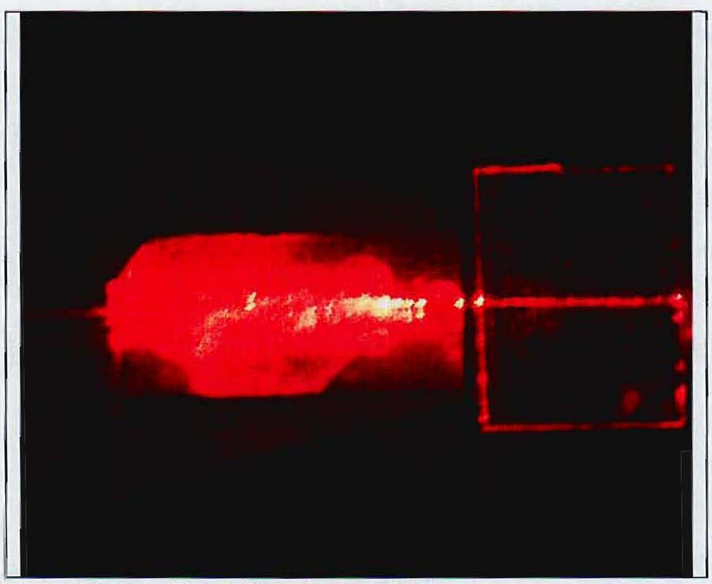


Figure 12 Light coupled into the Cr-diffused waveguide

In summary, we demonstrated the formation of Cr diffused sapphire waveguides. The Cr^{3+} ions are incorporated into the sapphire planar waveguide by thermal diffusion. After diffusion, the surface of the Cr doped sapphire is very smooth, which is suitable for devices fabrication. The light at 632.8 nm is coupled into the Cr-diffused planar waveguide. These results demonstrate that the potential applications of the Cr-diffused waveguide in integrated optical circuits.

One difficulty was obtaining multimode waveguides. This was accomplished by instead of diffusing the Cr into the sapphire at high temperatures, by ablating a ruby laser rod to place an amorphous layer of Cr:Sapphire and then re crystallizing the Cr:Sapphire. However further work is needed to optimize this approach.

Preliminary growths of wide bandgap semiconductors were also performed on the Cr:Sapphire waveguides. The materials were of high enough quality that they could support optical modes, in both the Cr doped sapphire layer and the ZnO wide band gap semiconductor. As shown in Figure 13 below.

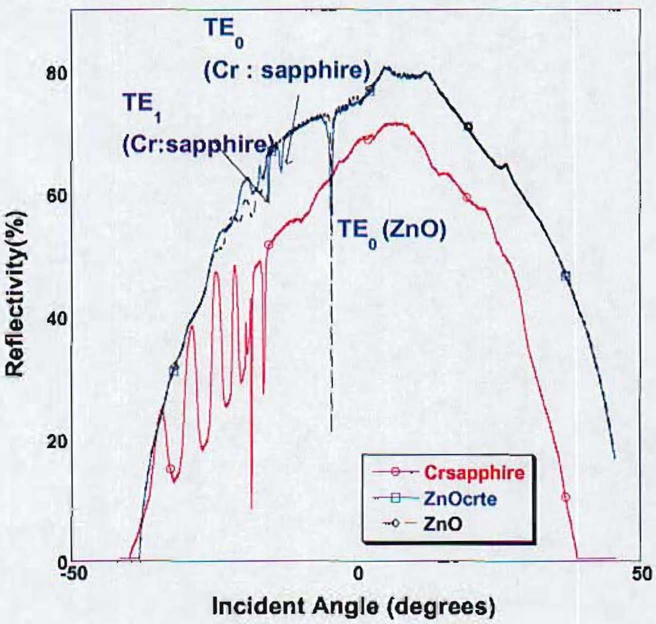


Figure 13: ZnO film deposited on Cr:Sapphire waveguide.

A variety of other studies that were performed that were related to the original proposal included the fabrication of GaN waveguides, and the simulation and design of GaN waveguide devices. Additionally multiple materials were investigated using the Prism coupling technique.

List of all Publications

(a) Papers published in peer-reviewed journals

1. Ji-Soo Park, Daryl W. Fothergill, Xiyao Zhang, Zachary J. Reitmeier, John F. Muth and Robert F. Davis, "Effect of Carrier Blocking Layers on the Emission Characteristics of AlGaN-based Ultraviolet Light Emitting Diodes" accepted to Japanese *Journal Applied Physics*. Special Issues on UV Emitters Sept. (2005)
2. H. L. Porter, A. L. Cai, J. F. Muth, and J. Narayan, "Enhanced photoconductivity of ZnO films Co-doped with nitrogen and tellurium" *Applied Physics Letters*, **86,** 211918, (2005)
3. H. L. Porter, C. Mion, A. L. Cai, X. Zhang, and J. F. Muth, "Growth of ZnO films on C-plane (0001) sapphire by pulsed electron deposition (PED)," *Materials Science and Engineering B-Solid State Materials for Advanced Technology*, vol. 119, pp. 210-212, 2005.
4. B. P. Cook, H. O. Everitt, I. Avrutsky, A. Osinsky, A. Cai, and J. F. Muth, "Refractive indices of ZnSiN2 on r-plane sapphire," *Applied Physics Letters*, vol. 86, 2005.
5. J. C. Roberts, C. A. Parker, J. F. Muth, S. F. Leboeuf, M. E. Aumer, S. M. Bedair, and M. J. Reed, "Ultraviolet-visible metal-semiconductor-metal photodetectors fabricated from InxGa1-xN (0 <= x <= 0.13)," *Journal of Electronic Materials*, vol. 31, pp. L1-L6, 2002.

(b) Papers published in non-peer-reviewed journals or in conference proceedings

1. (Invited) "Gallium nitride optoelectronic substrates for biological sensing", Muth, J.F.; Lasers and Electro-Optics Society, 2004. LEOS 2004. The 17th Annual Meeting of the IEEE Volume 1, 7-11 Nov. 2004 Page(s):292 - 293
2. A.L. Cai, J.F. Muth, M.J. Reed, H.L. Porter, C. Jin, and J. Narayan, 2002, Effect of Growth Temperature and Annealing on ZnO in "Progress in Semiconductors II--Electronic and Optoelectronic Applications", Editors: B.D. Weaver, M.O. Manasreh, C.C. Jagadish, S. Zollner, MRS Proceedings Volume 744
3. The Refractive Index and Other Properties of Doped ZnO Films, A.L. Cai, J.F. Muth, H.L. Porter, J. Narayan. Mat. Res. Soc. Symp. Proc. Vol. 764 (2003).

(c) Papers presented at meetings, but not published in conference proceedings

1. C3.21 Changes in the Ordinary and Extraordinary Refractive Indices For Doped ZnO Epitaxial Layers. Ailing Cai And John Muth, Hugh Porter And J. Narayan, Material Research Society Spring Meeting, San Francisco, April 21-25, 2003.

2. C7.6 Integrated Optical Pumping Of Ruby Substrates By InGan Led Grown On Cr:Sapphire. Andrew Oberhofer, John Muth, John Roberts, And Salah Bedair, Mason Reed, Material Research Society Spring Meeting, San Francisco, April 21-25, 2003.

3. E11.45 Optical Properties of II-IV-N_2 Semiconductors. John F Muth, Andrei Osinsky, Henry Everitt and Ivan Avrutsky, Material Research Society Fall Meeting, Boston, November 29-Dec 3, 2002.

4. F14.8 "Gallium Oxide Transparent Conducting Oxide Films by Deposited by Pulsed Electron Beam and Pulsed Laser Deposition Techniques." John Muth, Christian Mion, Jason Kekas and Ailing Cai, Material Research Society, Spring Meeting, San Francisco, March 28-April 1, 2005.

5. V6.2 "Gallium Oxide as a Host for Rare Earth Elements." John Muth, Praveen Gollokota, Anuj Dhawan, Yoga Saripalli, Leda Lunardi, Material Research Society, Spring Meeting, San Francisco, March 28-April 1, 2005.

6. DD6.3 "Analysis of Heat Transfer Limitations in III-Nitride Thin Films Grown on Non-Native Substrates." Christian Mion, Ji-Soo Park and John Muth, Material Research Society, Spring Meeting, San Francisco, March 28-April 1, 2005

7. "Pulsed Laser Depositon of Erbium and Europium Doped Gallium Oxide" Praveen Gollakota, Leda Lunardi, Anuj Dhawan, Yoga Saripalli, John Muth, Workshop on Global Perspectives in Frontiers of Photonics: Computational Imaging, Biophotonics and Nanophotonics Duke University, Durham NC, May 18-20, 2005

(d) Manuscripts submitted, but not published

1. "Red and Blue Dual Wavelength InGaN LED grown on Al2O3:Cr3+ (Ruby) Substrate", J.F. Muth, J.C. Roberts, A.E. Oberhofer, M. Reed, S.M. Bedair, submitted to Applied Physics Letters.
2. A. L. Cai, J. F. Muth, A. Osinsky, J. Q, Xie, J. W. Dong, "Refractive indices of A-plane ZnO thin films on R-plane sapphire", to be Submitted to Materials Science B.
3. A. L. Cai, J. F. Muth, A. Osinsky, J. Q, Xie, J. W. Dong, "Refractive indices of A-plane GaN thin films on R-plane sapphire", to be submitted to Applied Physics Letter.

(e) Technical reports submitted to ARO

None

(7) List of all participating scientific personnel showing any advanced degrees earned by them

Participating Personnel: (PhDs)

John Muth,
John Roberts,
Salah Bedair,
Mark Johnson,
Mike Gerhold

Students earning degrees who received support:

Andrew Oberhoffer(PhD),
Ailing Cai (PhD),
Hugh Porter (PhD),
Steven Bopp (M.S.)

Other students who interacted who will eventually receive degrees (PhD candidates)

Mason Reed,
Anuj Dhawan.

(8) Report of Inventions

No Patents Granted.

(10) Appendixes

none